8 Analysis of Other Ancillary Data

8.1 Ozone Carryover and Day-of-Week Phenomena – ARCO Building SCOS97

Abstract

Does Ozone Carryover Affect Day-of-the-Week Phenomena? Given substantially limited and discontinuous data aloft, in time and in space, we cannot resolve this question. Nevertheless, this work suggests a better question - how does carryover of ozone and aged pollutants aloft affect day-of-the-week ground level ozone phenomena. This limited analysis suggests that carryover of ozone has day-of-the-week influences. Without the effect of carryover, ground level ozone concentrations are usually reduced on Mondays. Aloft layers, some at least 2 days old, affected ground level ozone concentrations.

8.1.1 Introduction

Until recently, Saturday was the day-of-the-week with the highest peak concentration of ambient ozone in the South Coast Air Basin (SoCAB) [*Austin & Tran*, 1999; *Winer & Blier*, 1999; *Winer & Blier*, 1996]. Sunday now appears to have replaced Saturday as the day-of-the-week with the highest peak concentration of ambient ozone in the SoCAB (*Austin & Tran*, 1999; *Winer & Blier*, 1999). The Air Resources Board (ARB) "Weekend Weekday Work Plan" (*Croes*, 1999) identifies potential causes of the Day-of-the-Week changes in ambient ozone concentrations. One hypothesis is that overnight carryover of pollutants from Friday evening traffic does impact Saturday and Sunday ozone photochemistry. For this to be true, carryover of ozone, apparent in changes of ozone concentrations aloft from one day to the next, should experience day-of-the-week variations. Without the impact of ozone layers aloft, ozone concentrations at ground level should decline from the previous day's level. Two-day old ozone layers aloft could impact ground level ozone concentrations. We report evidence of these three phenomena.

8.1.2 Methodology

During the 1997 Southern California Ozone Study (SCOS97), we operated a Dasibi 1003-AH ultraviolet photometry ozone analyzer at the Atlantic Richfield Company (ARCO) headquarter tower in central Los Angeles (198 meters above mean sea level (msl)). On July 18, 1997, an ARB audit team invalidated these data because the temperature of the analyzer compartment was not recorded, the data logger was inoperative, and the inlet was not at least one (1) meter away from the building; the analyzer output deviated 8% high from the true value. For these reasons, the data did not meet federal Environmental Protection Agency (EPA) guidelines. We believe these ozone analyzers do not produce erroneous data due to high room temperature and have confidence in the ozone data from ARCO tower. The South Coast Air Quality Management District operates a routine monitoring site located inside a Los Angeles Department of Water and Power facility on North Main Street (LANM). The ARCO tower is roughly one mile west-south-west of LANM. The data from these two sites provide a rough but continuous idea of the lowest portion of ozone layers aloft. The LANM data met the federal EPA quality guidelines.

During SCOS97, balloons with potassium iodine total oxidant instruments, and temperature and relative humidity capacitance probes were launched from seven locations. University of Southern California's (USC) Hancock Foundation Building, located south of Central Los Angeles, was one site location. Balloons were launched at 0200, 0800, 1400, and 2000 hours local time. The USC site is located 4 miles southwest of LANM. The USC data provide a snapshot-in-time view of the vertical profile of ozone concentrations aloft. The USC ozone balloon data have passed "level 1" quality guidelines [*Fujita* et. al., 1999].

8.1.3 Results & Discussion

On average there was a 10 parts per billion volume (ppbV) difference between concentrations at ARCO tower and LANM - 75th percentile values were significantly above the average and there were negative 25th percentile values. These differences were not merely due to differences in measuring instruments and are indicative of movement of ozone layers downwards. On average, there were higher ozone concentrations even less than 100 meters above ground level (agl) than at ground level.

Looking at these differences on a day-to-day coupled basis, correlation between these differences suggests that the Friday to Saturday and Sunday to Monday transitions occur very differently than other day-to-day transitions. Accepting that during most days of the week ozone mixes downwards affecting ground level concentrations, Monday and Saturday ground level ozone concentrations benefit differently from carryover (Table 8.1-1). Based on the foregoing, interaction of ozone aloft (100 meters) with ground level concentrations has a day-of-the-week influence. To further investigate this influence at ARCO and LANM during SCOS97, we reviewed how hourly ozone concentrations from one day are related to the next day. These tables for ARCO and for LANM suggest a strong relationship between one day’s hourly ozone concentration profile and the next. However, differences (ARCO minus LANM) for each hour from one day to the next day (Table 8.1-2) offered a different perspective.

When there were significant changes in the ozone aloft profile (lightly shaded squares in Table 8.1-2; R^2=0.01 to 0.03), such changes were confined to Fri-Sat (2), Sat-Sun (1), Sun-Mon (1), and Wed-Th (1). We noted previously that Sunday to Monday and Friday to Saturday showed changes in ozone aloft different from other days (Table 8.1-1). Otherwise, there was significant continuity (darkly shaded squares in Table 8.1-2; R^2=0.8 to 0.9) of ozone profiles aloft spread throughout the days of the week Th-Fri (1), Sat-Sun (1), Sun-Mon (2), Mon-Tue (3), Tue-Wed (2), Wed-Th (1). Carryover generally depends on continuation of ozone aloft to build stronger aloft layers; significant correlation changes may signal removal/dispersion of aloft layers. The build-up of stronger aloft layers seemed not to vary by day-of-the-week. However, removal/exhaustion of ozone layers aloft varied strongly by day-of-the-week.

To explore the magnitude of the day-to-day changes, we assembled daily maximum-hour concentrations for the LANM site during SCOS97. Sunday was the highest ambient ozone day of the week at the LANM site during SCOS97. We noted significant ozone highs (>80 ppbV - red) to lows (60 ppbV or less - blue) in Table 8.1-3. Such changes are rare (4) and occur Sunday to Monday (2) and Tuesday to Wednesday (2). Most extreme of these day-to-day changes (>50 ppbV- underlined) coincide with very low correlation between day-to-day ozone aloft profiles (0.01, 0.23, and 0.13 R^2 in order of appearance in Table 8.1-3). Exhaustion of ozone layers aloft, expressed in weak day-to-day ozone aloft correlation, coincided with extreme changes in day-to-day ozone. Two out of three such occasions occurred Sunday to Monday.

To examine how day-to-day changes in ground level ozone and in ozone layers aloft may be related, Table 8.1-2 is referenced again but we shaded the day-to-day couples with ground level ozone concentration reductions of 30 parts per billion volume (ppbV) or more (Table 8.1-4). Such reductions occurred from Sunday to Monday (5), Monday to Tuesday (1), Tuesday to Wednesday (1), and Wednesday to Thursday (1). No such reduction occurred from Thursday to Sunday. Sunday to Monday correlation were either high (R^2 = 0.8 or higher) or low (0.13 or 0.01). Other days of the week had moderate correlations (R^2 of 0.52, 0.61, and 0.63).

The high R^2 indicates that layers aloft did not significantly alter ground level concentrations and Monday's fresh nitrogen oxide emissions significantly reduced ground level ozone concentrations. The low R^2 indicates a total exhaustion of aloft profiles as they existed the day before. Both phenomena indicate that on Mondays, unlike other days of the week, when ozone concentrations suffer significant decreases, carryover is absent. Because increases of ground level ozone from day to day was of interest, we present Table 8.1-2 with shaded cells denoting 20 ppbV or more increases of LANM ozone from day to day (Table 8.1-5).

Such increases occurred from Thursday to Friday (2), Friday to Saturday (2), Saturday to Sunday (4), and Tuesday to Wednesday (1). R^2 values vary widely (0.14 to 0.85) but they are never very low (0.01 to 0.03). Decreases in ground level ozone concentrations showed influence of carryover manifested in either ozone aloft profiles not changing at all from day to day or changing significantly. Carryover seen in strong or weak correlation between ozone aloft profiles had a day of the week influence. Moreover, ground level ozone concentrations declined more significantly in the absence of contribution from ozone aloft. There were indications that ozone aloft profiles had a day-of-week relationship and that the absence of carryover was related to significant reductions in ground level ozone concentrations. The remaining issue was to demonstrate that carryover processes could take place during two or more days of atmospheric chemistry.

These are implication of analyses of only the data from the first 100 meters of ozone aloft profile at a source site during SCOS97. Continuous aloft data at more sites and for a more significant fraction of the aloft profile would provide a better understanding of carryover. During SCOS97, ozone balloon data provided a snap shot of the entirety of the aloft profile. Looking at these snapshots in view of the evolution of ground level concentrations provided another piece of anecdotal analysis to focus on multi-day carryover events.

It is conceptually convenient to separate the closest layer to the ground (up to 500 to 700 meters agl) as the compartment in the atmosphere most susceptible to interaction with the ground-based emissions and atmospheric chemistry associated with these emissions. Due to the loss of daytime atmospheric chemistry, the influence of the nocturnal boundary conditions, and nighttime emissions of nitrogen oxide, this reservoir layer may be reduced to very low concentrations nocturnally. During the day, much of ozone buildup related to that day's atmospheric chemistry fills this compartment first. For further convenience we have called this layer the Reservoir (Figure 8.1-1).

There are a series of layers of ozone above the reservoir (from 500-700 up to 3,000-4,000 meters agl) that can be viewed for conceptual convenience as one alpha layer. These layers are influenced by flow of ozone from the reservoir (daytime) and from above the alpha layer and in turn can influence ozone in the reservoir. Ozone concentrations are not significantly reduced at night because nighttime ground deposition and nitrogen oxide emissions have no significant impact on these layers. Thus, the alpha layer may exist at high concentrations for several days. Although their interaction with the reservoir and their consequent impact on ground level ozone concentrations depend entirely on the meteorological factors, the ozone concentration load they contain depends entirely on reservoir ozone formation processes that occurred one or several days before.

There are yet a third series of ozone layers above the alpha layer (from 3,000-4,000 up to 6,000+ meters agl) that can be viewed for conceptual convenience as one beta layer. These layers can be influenced by flow of ozone from the alpha and reservoir layers and in turn may influence the alpha and reservoir layers, more importantly they have a regional nature and speak more to the background ozone concentrations. It is important to keep in mind the three-dimensional nature of ozone layers aloft in the complex southern California Bight where land-sea interactions play a critical role in developing regional meteorology and atmospheric chemistry. Designation of these layers is only for convenience and cannot reflect the full complexity of ozone aloft phenomena.

Nevertheless, a series of USC balloon snapshots of the ozone vertical profile is indicative of interaction of the alpha layers with ground levels. In particular, these interactions are noted for the August 22nd to 23rd high ozone episode (Friday to

Saturday). By the early morning hours (0200) before Saturday, August 23rd, the alpha layer had perhaps 60 to 80 ppbV of ozone within it while the reservoir was essentially exhausted. While the reservoir grew by atmospheric chemistry of morning emissions (0800 hours snapshot), boundary conditions improved to permit more mixing and by 1400 hours the alpha layer seemed to have mixed with the reservoir. There were indications that carryover affected the ground level concentrations (Figure 8.1-2).

The USC snapshots from September 4 (Thursday) to 6 (Saturday) indicate that such carryover can take place over more than one day. A narrow alpha layer containing roughly 80 ppbV of ozone began on Thursday and was reinforced during Thursday, existed during Friday and weakened somewhat but did not mix down, and finally mixed down on Saturday and was entirely exhausted contributing to a peak of 66 ppbV at LANM. Carryover from Thursday affected Saturday's ground level ozone concentrations (Figure 8.1-3).

These limited analyses overlook the fact that aloft photochemistry is rather like ground level processes in that ozone, reactive organic gases, and nitrogen species are part of a complex set of chemical interactions that continue away from emission sources. These limited analyses also ignore the fact that these snap shots are indications of a three-dimensional phenomena that encompasses the entirety of the southern California Bight and includes land-sea interactions and air parcel transport processes. Nevertheless, there is evidence that aloft layers affected ground level concentrations and that such carryover can occur over more than one day.

8.1.4 Conclusions

There are indications that during SCOS97 and for a source area, carryover of ozone had day-of-the-week influences and without the effect of carryover, ground level ozone concentrations are usually reduced. There are also indications that aloft layers, some at least 2 days old, affected ground level concentrations.

8.1.5 Recommendations

This type of analysis is critical to evaluate regional air pollution transport assessment. With the expansion of transport assessment to trans-national air pollution transport (to and from Mexico and to and from People’s Republic of China), these analyses are even more relevant and important for California. Continuous ozone aloft measurements using light detection and ranging during several ozone seasons would provide a database to properly conduct this critical analysis. Continuous measurements of aged hydrocarbons during several ozone seasons using tethered balloons offshore and in the Mojave Desert and Salton Sea air basins would also help this type of critical analysis.

8.1.6 References

Austin J., and Hien Tran (1999) "A characterization of the weekday-weekend behavior of ambient ozone concentrations in California," http://arbis.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm, June 23.

Blier, W., and Arthur Winer (1999) "Analysis of Weekday/Weekend Differences in Ambient Air Quality and Meteorology in the South Coast Air Basin," Air Resources Board Contract No. 95-334, June.

Blier, W., and Arthur Winer (1996) "Characterization of Ozone Episodes in the South Coast Air Baisin: Effects of Air Parcel Residence Time and Weekend/Weekday Differences," Air Resources Board Contract No. 93-316, June.

Croes, B. (1999) "Workplan for Weekend Effect Research" http://arbis.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm, June 23.

Fujita, E., M. Green, R. Keislar, D. Koracin, H. Moosmuller, and J. Watson (1999) "SCOS97-NARSTO 1997 Southern California Ozone Study and Aerosol Study, Volume III: Summary of Field Study," Air Resources Board Contract No. 93-326, February.

Table 8.1-1. Correlations of Day-Pair Ozone Concentration Differences at and between ARCO and LANM during SCOS97

	Difference between ARCO & LANM Difference	Difference at ARCO	Difference at LANM
Day-Pair	**Correlation Coefficient**		
THURSDAY-FRIDAY	**0.67**	**0.74**	**0.80**
FRIDAY-SATURDAY	***0.49***	***0.69***	**0.81**
SATURDAY-SUNDAY	**0.73**	**0.82**	**0.87**
SUNDAY-MONDAY	***0.58***	***0.68***	**0.83**
MONDAY-TUESDAY	**0.79**	**0.70**	**0.81**
TUESDAY-WEDNESDAY	**0.55**	**0.63**	**0.64**
WEDNESDAY-THURSDAY	**0.53**	**0.66**	**0.78**

Table 8.1-2. Correlation of Hourly ARCO-LANM Differences for Day-to-Day Pairs

	Multiple R for Relationship between Daily ARCO-LANM Differences						
Week	Th-Fri	Fri-Sat	Sat-Sun	Sun-Mon	Mon-Tue	Tue-Wed	Wed-Th
3-Jul		**0.29**	**0.18**	**0.01**	**0.26**	**0.84**	**0.35**
10-Jul	**0.34**	**0.14**	**0.31**	**0.14**	**0.48**	**0.17**	**0.30**
17-Jul	**0.23**	**0.39**	**0.01**	**0.36**	**0.07**	**0.30**	**0.67**
24-Jul	**0.12**	**0.09**	**0.14**	**0.10**	**0.68**	**0.09**	**0.52**
31-Jul	**0.68**	**0.32**	**0.45**	**0.39**	**0.68**	**0.52**	**0.14**
7-Aug	**0.28**	**0.48**	**0.27**	**0.43**	**0.71**	**0.35**	**0.03**
14-Aug	**0.22**	**0.01**	**0.14**			**0.60**	**0.60**
21-Aug					**0.78**	**0.75**	**0.60**
28-Aug	**0.66**	**0.67**	**0.64**	**0.91**	**0.85**	**0.66**	**0.79**
4-Sep	**0.81**	**0.58**	**0.56**	**0.33**	**0.57**	**0.51**	**0.56**
11-Sep	**0.59**	**0.40**	**0.62**	**0.86**	**0.38**	**0.90**	**0.44**
18-Sep	**0.71**	**0.43**	**0.85**	**0.78**	**0.63**	**0.23**	**0.52**
25-Sep		**0.51**	**0.65**	**0.13**	**0.86**	**0.74**	**0.61**
2-Oct	**0.40**	**0.32**	**0.10**	**0.69**	**0.89**	**0.79**	**0.13**
9-Oct	**0.50**	**0.18**	**0.31**	**0.60**	**0.48**	**0.73**	**0.85**
16-Oct		**0.01**	**0.31**				

Table 8.1-3. Daily maximum- hour ozone concentrations at Los Angeles – N. Main

LANM Peak Ozone Concentration (ppb)							
Week	Fri	Sat	Sun	Mon	Tue	Wed	Th
3-Jul	102	87	98	46	45	46	48
10-Jul	35	37	56	44	40	44	60
17-Jul	43	39	46	51	22	56	40
24-Jul	50	46	57	49	41	55	58
31-Jul	61	85	96	82	90	59	52
7-Aug	46	38	34	34	40	54	61
14-Aug	46	37	59		17	33	43
21-Aug	56	80	87	45	59	70	62
28-Aug	60	86	120	86	73	68	73
4-Sep	36	66	64	56	61	58	33
11-Sep	41	56	75	42	32	35	59
18-Sep	29	38	73	81	82	31	3
25-Sep	36	83	111	60	66	68	28
2-Oct	47	59	59	36	31	43	35
9-Oct	30	33	36	40	23	26	
16-Oct	53	56	57				

Table 8.1-4. Correlation of Hourly ARCO-LANM Differences for Day-to-Day Pairs

Day to Day Increases of 30 ppbV or More*							
Week	Th-Fri	Fri-Sat	Sat-Sun	Sun-Mon	Mon-Tue	Tue-Wed	Wed-Th
3-Jul		0.29	0.18	0.01	0.26	0.84	0.35
10-Jul	0.34	0.14	0.31	0.14	0.48	0.17	0.30
17-Jul	0.23	0.39	0.01	0.36	0.07	0.30	0.67
24-Jul	0.12	0.09	0.14	0.10	0.68	0.09	0.52
31-Jul	0.68	0.32	0.45	0.39	0.68	0.52	0.14
7-Aug	0.28	0.48	0.27	0.43	0.71	0.35	0.03
14-Aug	0.22	0.01	0.14			0.60	0.60
21-Aug					0.78	0.75	0.60
28-Aug	0.66	0.67	0.64	0.91	0.85	0.66	0.79
4-Sep	0.81	0.58	0.56	0.33	0.57	0.51	0.56
11-Sep	0.59	0.40	0.62	0.86	0.38	0.90	0.44
18-Sep	0.71	0.43	0.85	0.78	0.63	0.23	0.52
25-Sep		0.51	0.65	0.13	0.86	0.74	0.61
2-Oct	0.40	0.32	0.10	0.69	0.89	0.79	0.13
9-Oct	0.50	0.18	0.31	0.60	0.48	0.73	0.85
16-Oct		0.01	0.31				

* Shaded Areas with 30 ppbV Day-to-Day Decrease at LANM

Table 8.1-5. Correlation of Hourly ARCO-LANM Differences for Day-to-Day Pairs

Multiple Correlation Coefficients between Daily ARCO-LANM Differences

Day to Day Decreases of 20 ppbV or More*

Week	Th-Fri	Fri-Sat	Sat-Sun	Sun-Mon	Mon-Tue	Tue-Wed	Wed-Th
3-Jul		0.29	0.18	0.01	0.26	0.84	0.35
10-Jul	0.34	0.14	0.31	0.14	0.48	0.17	0.30
17-Jul	0.23	0.39	0.01	0.36	0.07	0.30	0.67
24-Jul	0.12	0.09	0.14	0.10	0.68	0.09	0.52
31-Jul	0.68	0.32	0.45	0.39	0.68	0.52	0.14
7-Aug	0.28	0.48	0.27	0.43	0.71	0.35	0.03
14-Aug	0.22	0.01	0.14			0.60	0.60
21-Aug					0.78	0.75	0.60
28-Aug	0.66	0.67	0.64	0.91	0.85	0.66	0.79
4-Sep	0.81	0.58	0.56	0.33	0.57	0.51	0.56
11-Sep	0.59	0.40	0.62	0.86	0.38	0.90	0.44
18-Sep	0.71	0.43	0.85	0.78	0.63	0.23	0.52
25-Sep		0.51	0.65	0.13	0.86	0.74	0.61
2-Oct	0.40	0.32	0.10	0.69	0.89	0.79	0.13
9-Oct	0.50	0.18	0.31	0.60	0.48	0.73	0.85
16-Oct		0.01	0.31				

* Shaded Areas with 20 ppbV Increase Day to Day at LANM.